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SEAWATER INTRUSION AND NITRATE POLLUTION IN COASTAL AQUIFER OF MARATHON BASIN

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Abstract

The overexploitation of groundwater and groundwater salinization cause quantitative and qualitative degradation of the water resources. The objectives of this research are to identify and investigate the extent of seawater intrusion and nitrate pollution into the coastal plain of Marathon in Eastern Attica, Greece. In the frame of this, 25 groundwater samples were collected in October 2014 from the study area and analyzed regarding the main parameters that indicated salinization of the aquifers. Specifically, water chemical analyses were carried out and statistical analyses regarding spatial distribution were performed. The results demonstrated increased values of the parameters which can be associated with seawater intrusion. Considering and evaluating the results from the chemical analyses it is obvious that seawater intrusion takes place in the area. Furthermore, the average concentration of NO_3^- was 44.16mg L^{-1} and this can be attributed to overexploitation of coastal aquifer for agricultural activities.
Key words: *Hydrochemistry, Hydrogeology, Pollution, Groundwater.*

Περίληψη

Η υπεράντληση των υπογείων υδάτων και η υφαλμύριση οδηγεί σε ποσοτική και ποιοτική υποβάθμιση των αποθεμάτων νερού. Οι στόχοι αυτής της μελέτης είναι να εντοπιστεί και να διερευνηθεί το φαινόμενο της υφαλμύρισης και νιτρορύπανσης στην παράκτια πεδιάδα του Μαραθώνα στην Ανατολική Αττική. Για το σκοπό αυτό, 25 δείγματα υπόγειων υδάτων συλλέχθηκαν κατά την περίοδο του Οκτωβρίου 2014 από την περιοχή μελέτης και αναλύθηκαν ορισμένες παράμετροι που σχετίζονται με την υφαλμύριση των υδροφορέων. Συγκεκριμένα, διεξήχθησαν χημικές αναλύσεις υδάτων, στατιστική επεξεργασία και χάρτες χωρικής κατανομής. Τα αποτελέσματα έδειξαν αυξημένες τιμές των παραμέτρων που μπορούν να αποδοθούν στη διείσδυση θαλασσινού νερού. Από την ανάλυση και κατανόηση των χαρακτηριστικών της ποιότητας των υπόγειων υδάτων του Μαραθώνα, είναι σαφές ότι η περιοχή βρίσκεται υπό καθεστώς θαλάσσιας διείσδυσης. Επιπλέον, η μέση συγκέντρωση NO_3 ήταν 44.16 mgL^{-1} και αυτό μπορεί να αποδοθεί στην υπερεκμετάλλευση των παράκτιων υδροφορέων για γεωργικές δραστηριότητες.
Λέξεις κλειδιά: *Υδροχημεία, Υδρογεωλογία, Ρύπανση, Υπόγεια νερά.*

1. Introduction

Water management of coastal aquifers is one of the major challenges of the modern world, because it is inextricably linked to the economy of the coastal areas. The phenomenon of seawater intrusion constitutes a special case of salinization which affects the quality of coastal aquifers. Almost all the cases of seawater intrusion that are recorded were caused by human activities and especially by the intense over pumpingin coastal areas. The overexploitation of groundwater results in the quantitative and qualitative degradation of the water reservoirs.

This study investigates the phenomenon of seawater intrusion into the coastal plain of Marathon, Eastern Attica, Greece. The research area shows great interest because it is a typical case of intense human intervention. It is located in the Northeastern part of the province of Attica and is bordered to the North by the mountainous regions of Kotroni, Strati and Terokorfi, to the West by Mountain Penteli, to the East by the mountainous regions of Drakonera and Mytikas, and to the Southeast by the Kynosoura peninsula (Figure 1).

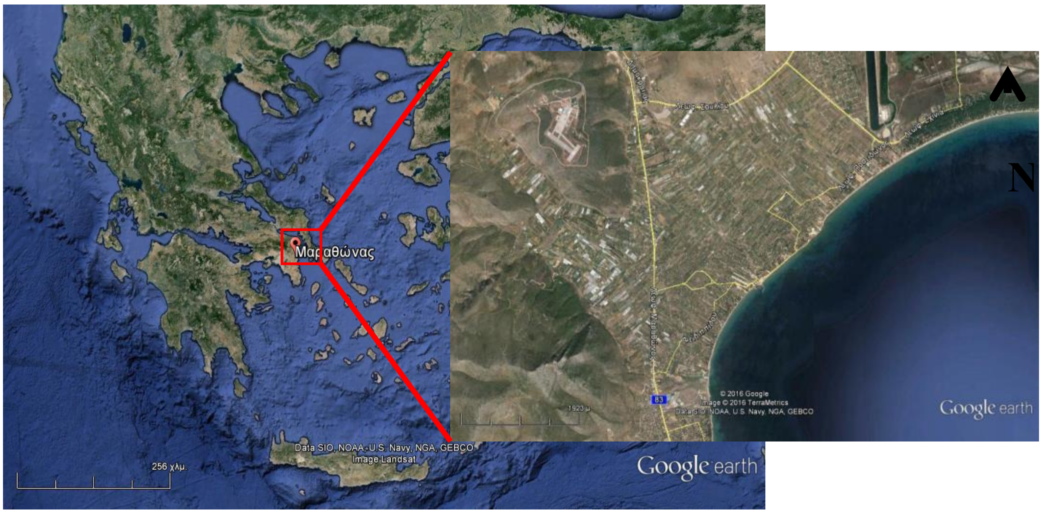

Figure 1- Location of the study area.

2. Materials and Methods

2.1. Geology - Hydrogeology

In Eastern Attica, and more specifically, in the wider Marathon area, there are four different geological units (Pavlopoulos *et al.*, 2002). These are (from the lowest to the highest):

- ✓ Almyropotamos unit that constitutes the indigenous unit of the area,
- ✓ Unit of Recent Greek Tectonic Cover.
- ✓ Unit of Afidnon - Tourkovounia.
- ✓ Unit of Mavrinoras – Katsimidiou. Regarding the Lithology, the area is consisted by marbles, schists, quaternary and Neogene deposits. The marbles cover almost all the hilly and mountainous area and the quaternary sediments cover most of the growth in the plain of Marathon.

In the area of interest, two types of aquifers are developed, the karstic and alluvial aquifers. In carbonate formations, the flow of groundwater is through karst pipes and cracks and is always controlled by impermeable schists occurrences, that interfere in the entire carbon mass. In recent deposits, a circulation of the groundwater via the porous grains is observed, where the stratigraphic structure allows. The schists, mainly, and Neogene marl deposits are practically impervious formations. The presence of schists controls the groundwater flow in carbonate formations and thus they are creating either partially, or completely isolated carbon units, or in combination with faults, new routes of karstic water.

The karstic aquifers in marble unit of Almyropotamos may be linked to the aquifer of the lower marble of Penteli. The marbles of Almyropotamos unit are showing intense karstification. The aquifer is located far from the sea. Also, it is possibly due to the interference of schist intercalations in marbles the development of some local individual water storage, but the main discharge of the karst system is through the Makaria spring of Kato Souli.

2.2. Meteorological Data

The climate of Marathon basin is typically semi-dry Mediterranean. Mostly, rainfall is observed during the cold season, as in the summer there are many drought periods. Meteorological data from the water supply company (Athens Water Supply and Sewerage Company -EYDAP S.A.) was evaluated from the nearest station in the study area: Marathon (in the period 1986-1997). The average annual rainfall was estimated at about 588.9 mm. During the period from June to September, the average monthly rainfall is lower than 20 mm per month resulting in negligible natural recharge of the aquifers. The average annual temperature is 17.4˚C. Figure 2 shows the temperature - precipitation diagram resulting from a combination of precipitation and temperature data. From this diagram, it seems that the wet season starts from mid-October and ends mid-March, while the dry season starts from mid-March and ends in mid October. The temperature - precipitation diagram confirms the dry climate of the region with relatively low rainfall and high temperatures during the dry season.

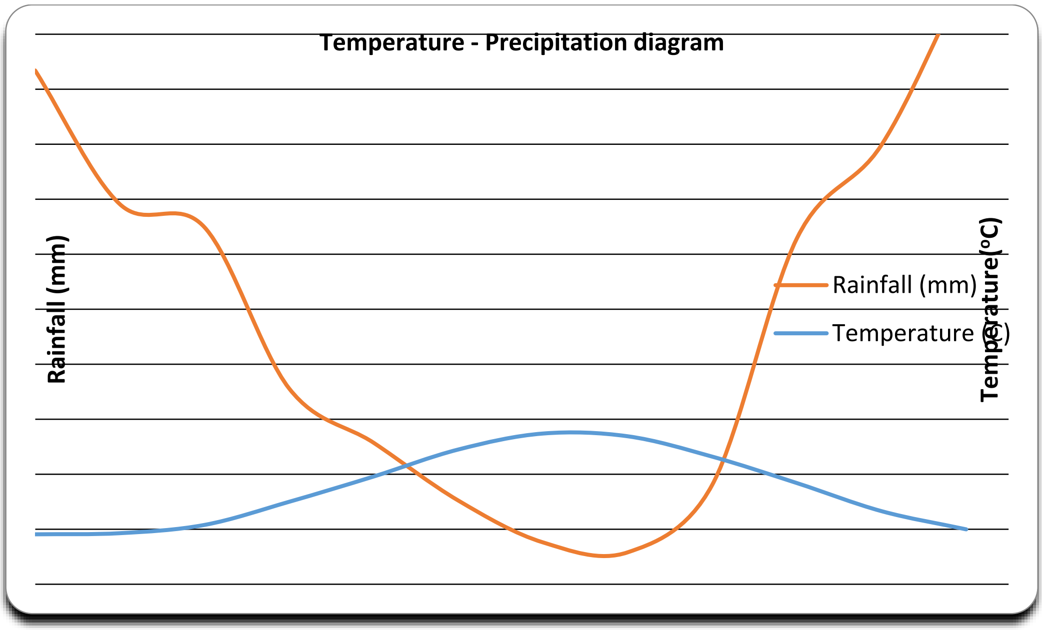

Figure 2 - Temperature - Precipitation diagram from Marathon station (in period 1986-1997).

2.3. Sampling and Analysis

Sampling of groundwater was carried out in October of 2014. This is the last month of the dry season, as the natural recharge is decreased. During the summer season, groundwater pumping for agricultural and potable uses is intense, so the water table is expected to be lower. Sampling sites were selected based on anthropogenic activities, in plain of Marathon.

Two water samples were taken from each site or well. One sample was used for the analyses of major anions and cations. This sample was stored in a vial polyethylene, which was flushed first with deionized water, and this was rinsed several times with the water sample, it was preserved in a cool, dark place, until it was transferred to the laboratory. The second sample was related to in situ measurements of unstable physicochemical parameters of water, as electrical conductivity measurements (EC), pH and temperature. These measurements were done with the portable instruments of the Laboratory of Engineering Geology and Hydrogeology, School of Mining Engineering - Metallurgy of the National Technical University of Athens. Totally 25 samples were collected in winter time.

3. Results and Discussions

3.1. Composition of major ions

The descriptive statistics of various chemical constituents and the ionic ratios for the 25 samples are presented in table 1. As shown in the table, all samples have values of EC> 1000 μS cm^{-1}, which means that all measurements are over the limits of fresh water in accordance with Directive the European Union. The seawater intrusion is also indicated by the high concentrations of Cl^- and Na^+. Specifically, the average concentrations of Cl^- were >500 mg L^{-1} when the usual values are < 10 mg L^{-1} in wet areas and < 100 mg L^{-1} in dry areas (Kallergis, 2000) and the average concentrations of Na^+ were> 200 mg L^{-1} when the usual values are < 20 mg L^{-1}. The nitrate concentrations are also considered high and over the acceptable limits of 50 mg L^{-1}. The spatial distribution of nitrates is higher in the areas that agricultural activities are taken place. Finally, ionic ratios Na / Cl and BEX (Base Exchange Index) confirm the seawater intrusion regime in the Marathon Basin. Specifically, all values of the ratio Na / Cl are < 0,876 indicating salinization in the aquifer. BEX is proposed by Stuyfzand (1986, 2008) and is given by the formula:

$$BEX = (Na^+ + K^+ + Mg^{2+}) - 1.0716 \times Cl^- \text{ (all in meq } L^{-1}\text{)}$$

When the index value is positive, it indicates recharge process and when it is negative, it indicates salinization conditions. Almost all values are negative. Koumantakis *et al.* (1993), Melissaris and Stavropoulos (1999) and Fotopoulos (2004) have confirmed the seawater intrusion inthe study area. Specifically, the average values of all parameters are higher in the period of October 2003 (Table 1), according to the study of Fotopoulos (2004). The elements which are associated with seawater intrusion (EC, Cl^-, Na^+) show a slight decrease in their concentration, while the nitrate pollution has decreased considerably. As shown, the qualitative situation of coastal aquifer in Marathon basin has improved in recent years.

The correlation coefficient of the studied parameters is shown in Table 2. A significant correlation is observed between EC and Cl^- (0.942) and between Na^+ and Cl^- (0.956), due to seawater intrusion. There are strong correlation between EC - Cl^- and Na^+ - Cl^- as it is shown in the Figure 3. From the data obtained, concentration of calcium ions is much lower compared to chloride ions which can be an indication of calcium removal as a result of calcite precipitation. Precipitation takes place during the cation exchange process which is the later effect from the seawater intrusion into the aquifer: Ca^{2+} in the aquifer matrix is exchanged with Na^+, the water becomes supersaturated with respect to calcite. The good correlation between Ca^{2+} and Mg^{2+} (0.926) is attributed to geogenic association and to the dissolution of calcite and dolomite. The main inputs of SO_4^{2-} and also NO_3^- into groundwater are derived from anthropogenic activities.

Table 1 - Descriptive statistics of samplings in the period of October 2014 (EC in μScm^{-1}, Cl^-, NO_3^-, Na^+,Ca^{+2}, Mg^{+2}, HCO_3^-, SO_4^{-2} inmgL^{-1} and ionic ratios of Na/Cl and BEX are unitless).

Parameter	October 2014 (25 samples)									
	EC	**Cl^-**	**NO_3^-**	**Na^+**	**Ca^{+2}**	**Mg^{+2}**	**HCO_3^-**	**SO_4^{-2}**	**Na/Cl**	**BEX**
Mean	2558.92	508.56	44.16	214	202.36	34.2	309.54	146.32	0.63	-3.08
Stdev[1]	1067.16	325.23	45.17	147,55	90.48	17.31	185.35	88.14	0.14	3.01
Max	4720	1220	175	494	382	69	763	340	0.84	0.36
Min	1025	75	4	38	102	11	67	41	0,33	-12.89
Quartile 1	1675	265	17	113	132	20	204,75	59	0.55	-4.2
Median	2380	380	24	144	171	32	265,5	155	0.7	-2.6
Quartile 3	3340	725	52	355	273	42	413,25	208	0.74	-1.18
Skewness	0.39	0.72	1.72	0.5	0.84	0.61	1,05	0.39	-0.59	-1.84
Kurtosis	2.11	2.49	5.3	1.71	2.37	2.2	3.56	1.99	2.29	7.32
October 2003(Mean)[2]	2972.11	699.61	140.59	425.61	256.75	54.76	318.64	167.39	-	-

[1] Standard deviation

[2] Fotopoulos (2004)

Table 2- Correlation matrix for all data.

	EC	**Cl^-**	**NO_3^-**	**Na^+**	**Ca^{+2}**	**Mg^{+2}**	**HCO_3^-**	**SO_4^{-2}**
EC	1							
Cl^-	**0.942**	1						
NO_3^-	0.254	-0.053	1					
Na^+	**0.877**	**0.956**	-0.221	1				
Ca^{+2}	**0.758**	0.549	**0.770**	0.365	1			
Mg^{+2}	**0.867**	0.711	0.626	0.558	**0.926**	1		
HCO_3^-	0.105	-0.209	**0.895**	-0.333	0.668	0.537	1	
SO_4^{-2}	**0.911**	**0.825**	0.351	**0.760**	**0.756**	**0.874**	0.271	1

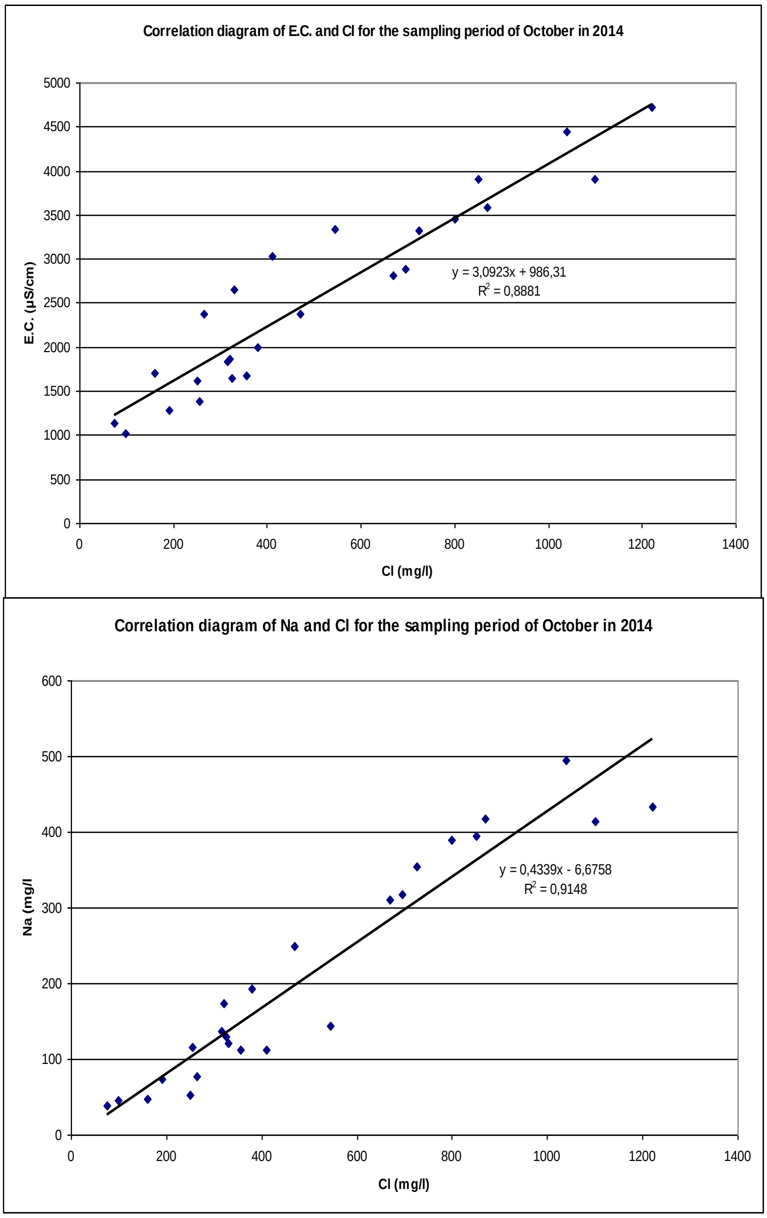

Figure 3 - Correlation diagrams of EC -Cl^- and Na^{+}- Cl^- for the sampling period of October 2014.

3.2. Spatial Distribution

The spatial distribution of some parameters is presented in figure 4. The statistical analysis of water sampling is shown in table 1. As it is observed by the parameters EC, Cl^-, Na^+ and the ionic ratios Na^+ / Cl^- and BEX (Figure 4), high values exceeding the acceptable limits, indicate seawater intrusion that are presented in the eastern part of the study area. On the west part of Marathon plain, concentrations and ionic ratios values are presented lower and it is likely to happen because the sampling locations are farther away from the coastline and on the other hand, there is possible recharge from the karstic mountain masses. The concentrations of nitrates are considered high, since they are over the indicative and the permissible limits of literature (~50 mg L^{-1}). In figure 4 (medium right), the spatial distribution of nitrate shows a specific point source pollution which spatially corresponds to an agricultural area. The intense agricultural activities are probably the main source of nitrate pollution in the research area.

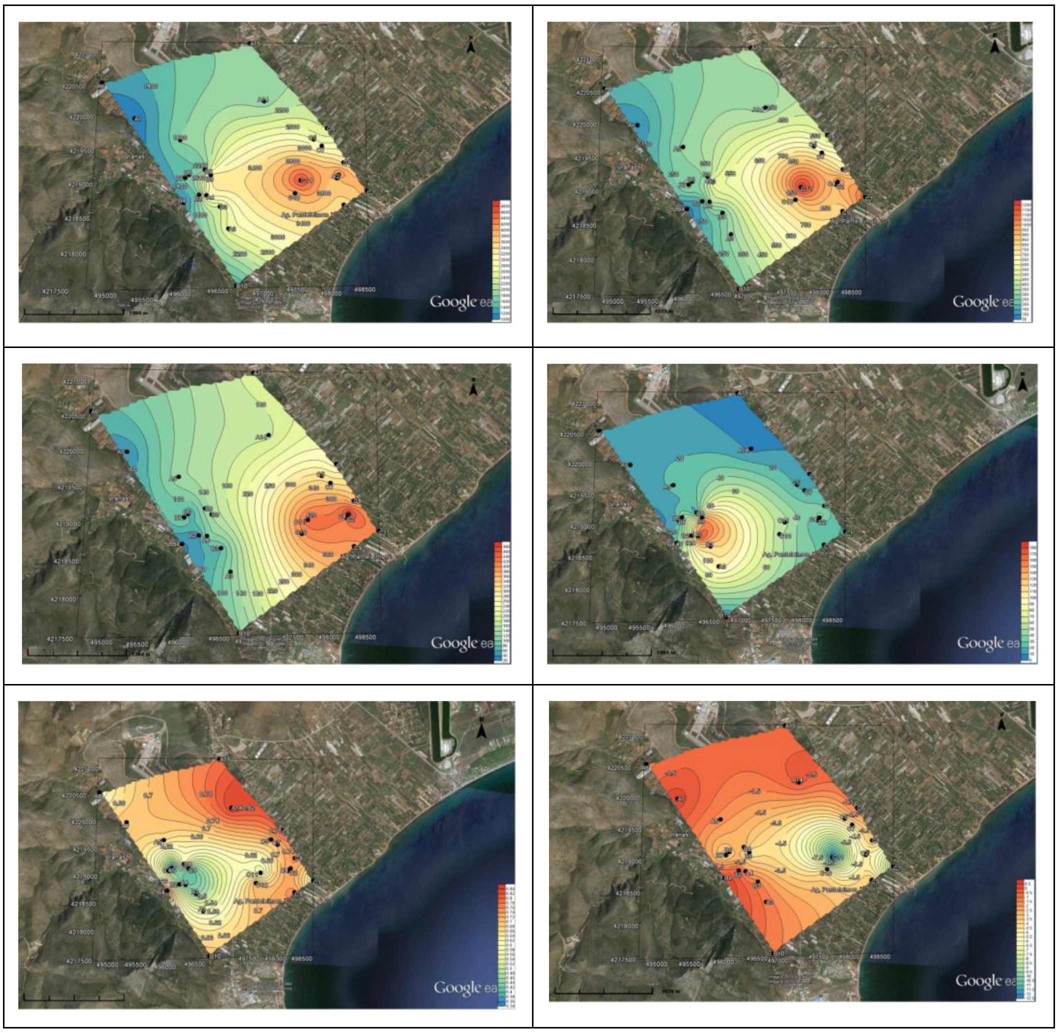

Figure 4 - Spatial distribution maps of EC in μS cm^{-1}(upper left), Cl^- in mg L^{-1}(upper right),Na^+mg L^{-1}(medium left), NO_3in mg L^{-1} (medium right), Na/Cl (lower left), BEX (lower right)for the period of October 2014.

3.3. Piper, Schoeller and Wilcox diagrams

As it is shown in Piper diagram in the lowland area of Marathon, two groups of water samples are distinguished. The first group (in the blue circle in Figure 5) is characterized as Ca-Na-Cl-HCO3 up to Na-Ca-Cl that definesthese samples as subsaline. The anions dominants are Cl-, while the corresponding cations are Na+. The second group is consisted of geoalkaline natural waters. More specifically, the water ischaracterized as acid carbonate - sulfates of formula Ca-HCO3-Cl. The anions dominants are HCO3, while the Ca2+ are in cations. The values of EC and chloride are very high in the coastal zone of the study area.

As it is observed in the Schoeller diagram, high concentrations of anions Cl- are distinguished, as seawater intrusion takes place in coastal and plain of Marathon.

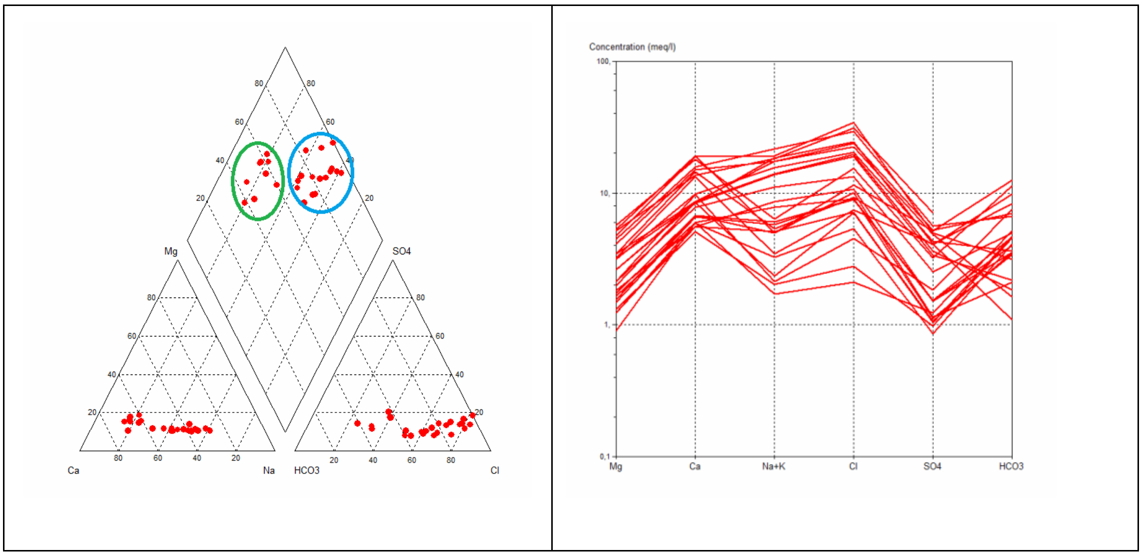

Figure 5 - Hydrochemical diagrams of Piper and Schoeller.

The United States Department of Agriculture (USDA) (1954) classifies irrigation water with respect to SAR. SAR is calculated from the following formula, all concentrations expressed in milli-equivalents per litre:

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}}$$

The waters having SAR values less than 10 are considered excellent, 10-18 as good, 18-6 as fair, and above 26 are unsuitable for irrigation use (US Salinity Laboratory Staff, 1954) (Table 3) (Fig. 6). Wilcox (1955) diagram (Fig. 6) is widely used and is especially implemented to classify groundwater quality for irrigation (Ebraheem *et al.*, 2012; Banoeng-Yakubo *et al.*, 2009; Ganyaglo *et al.*, 2011; Swarna Latha and Nageswara Rao, 2012; Mtoni *et al.*, 2013). The calculated SAR values range from 0.86 to 7.55 in groundwater in the study area and almost all samples fall into excellent class (Table 3). The USDA (1954) has also classified irrigation waters on the basis of electrical conductivity (EC) as indicated in Table 3.

According to USSL diagram (US Salinity Laboratory Staff, 1954), which is widely used for rating the irrigation waters, water can be grouped into 16 classes. It uses SAR (vertical axis) and specific conductance (horizontal axis) (Fig. 6) (Table 4). The conductivity (horizontal axis) is classified into low (C1), medium (C2), high (C3) and very high (C4) salinity zones. These zones (C1-C4) have the value of EC < 250, 250-750, 750-2.250 and >2.250 $\mu S\ cm^{-1}$, respectively. The SAR (vertical axis) is subdivided into four classes, with decreasing limiting values as EC increases: low (S1), medium (S2), high (S3) and very high (S4) sodium hazard. Significance of classes in relation to EC and SAR is presented in Table 4. The results show that 44% of all samples from the study area were graded as suitable for irrigation use, while 36% as unsuitable. 20% of samples were regarded as suitable under specific conditions. Groundwater samples classified as C3S1, C4S1 and C4S2 were the dominant classes.

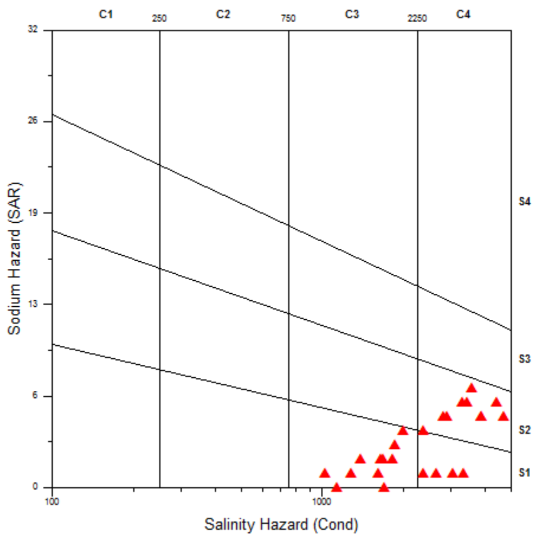

Figure 6 - Groundwater suitability for irrigation in the study area. Assessment was conducted using Wilcox (1955) diagram.

Table 3 - Classification of irrigation water according to USDA (1954).

Parameter	Range	Waterclass	Noof samples	%
SAR	<10	Excellent	25	100
	10 - 18	Good	0	0
	18 - 26	Doubtful	0	0
	>26	Unsuitable	0	0
EC ($\mu S\ cm^{-1}$)	100-250	Lowsalinitywater	0	0
	250-750	Mediumsalinitywater	0	0
	750-2250	Highsalinitywater	11	44
	>2250	Veryhighsalinitywater	14	56

Table 4 - Summary of groundwater classification based on USSL diagram.

No	Category	Noofsamples	Salinity/sodiumhazard	Statusforirrigation
1	C3-S1	11	High salinity hazard - low sodium hazard	Suitable
2	C4-S1	5	Very high salinity hazard - low sodium hazard	Suitableinspecificcondition
3	C4-S2	9	Very high salinity hazard - medium sodium hazard	Unsuitable

4. Conclusions

In the basin of Marathon, Eastern Attica, Greece, a hydrogeological research carried out in the period of October 2014. The hydrogeological and hydrochemical study in Marathon basin shows that the area is under seawater intrusion regime. The qualitative characteristics of groundwater haven't changed significantly during the last decades, as it is described in previous studies (Koumantakis *et al.*, 1993; Melissaris and Stavropoulos, 1999). Summarizing, EC expresses the total concentration of salts in the water and it is a measure of the quality of groundwater. The EC measured values range from 1025 μS cm^{-1} to 4720 μS cm^{-1}. All samples show EC > 1000 μS cm^{-1}, the minimum value is bigger than the target value of the European Union (~ 400 μS cm^{-1}). The presence of Cl^- usually reveals seawater intrusion into the aquifer and is directly connected with the high values of EC. The concentrations of Cl^- in the Marathon coastal plain are considered high, making explicit the qualitative degradation of the groundwater reserves in the study area. The normal Na^+ concentrations in groundwater are < 20 mg L^{-1}. However, concentrations of Na^+ in the study area are ranging from 38 mg $L^{-1}$to 494 mg L^{-1}. The increased concentration is probably due to contamination by seawater intrusion and possible ion exchange of Ca^{2+} and Na^+ because of seawater intrusion. Spatially, the sampling locations were close to the sea - in the east of the study area - showing the highest values of EC, Cl^- and Na^+. In addition, the spatial distribution of ionic ratios Na / Cl and BEX show high values in the eastern part of the study area, confirming the salination conditions.

The nitrates (NO_3^-) are derived from nitrogen compounds through complex processes such as ammonification and nitrification. These processes take place above groundwater level, especially in the soil where there are abundant organic material and oxygen. The nitrate is one of the forms of dissolved nitrogen which is highly mobile in groundwater. NO_3^- is the most prevalent contaminant and the large spread occurs due to agricultural activities such as nitrogen and nitrate fertilizers. Average value of NO_3^- was 44.16 mg L^{-1}, while 36% of collected samples exceeded the maximum permitted level (~ 50 mg L^{-1}). The concentrations of NO_3^- are considered high, but their detection is expected in the areas where there are agricultural crops. On the spatial distribution map of NO_3^-, a large point of source pollution is presented, which corresponds to agricultural area. West of the polluted area, an abrupt qualitative change is observed, which is likely due to natural recharge from meteoric water, while at the coastal region, of the Eastern region of the map, Neogene formations containing organic material contribute to the reduction of nitrate ions concentrations.

The hydrogeochemical results show that several processes determine major ionic composition of groundwater in the study area. The distribution pattern of major ions shows compositional variation in the groundwater samples. In general, the concentration of cations decreases in the order Na^+> Ca^{2+}>Mg^+ and of anions in the order Cl^-> HCO_3^-> SO_4^{2-}> NO_3^-. However, HCO_3^- dominates over Cl^- in some samples. Correlation analysis indicates that most of the ions are positively correlated. The reasonably good correlation among the ions, especially Na^+ and Cl^-, indicates that such ions are mainly derived from the same source of saline waters. This implies that the groundwater salinization process of the study area occurs near to the coastline associated with seawater.

In conclusion, the coastal plain of Marathon lies under seawater intrusion presenting high values EC, Cl^-, Na^+ and ionic ratios Na / Cl and BEX, as well as increased values of NO_3^- because of extensive farming activities (fertilizers, pesticides). The area is characterized from the overexploitation of the aquifers by overpumping because of irrigation land use. The salinity and sodium hazards of groundwater in Marathon basin were mainly classified as C3S1, C4S1 and C4S4, i.e., high salinity with low and medium sodium problems.

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